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STUDIES ON THE KINETICS OF THE REACTION OF PROPARGYL ALCOHOL WITH AQUEOUS FORMALDEHYDE SOLUTION

By RYO KIYAMA, JIRO OSUGI, KEIZO SUZUKI and YUTAKA KOMETANI

Introduction

The studies on the kinetics of the reaction of acetylene with aqueous formaldehyde solution were already reported in *This Journal*¹⁾. According to those works, it is possible to make butynediol synthesis from propargyl alcohol and formaldehyde in the following equation in the presence of a catalyst without the supply of acetylene. That is,



Moreover, the activation energy in the butynediol formation from propargyl alcohol and formaldehyde being relatively small, this reaction occurs at such a low temperature as the employment of autoclave is not needed. It was confirmed, in the previous work²⁾, that this reaction occurs under these conditions, but the reaction process has not been studied hitherto. Then, the following experiment under atmospheric pressure is performed from the standpoint of the chemical kinetics.

Experimentals

An aqueous solution of propargyl alcohol and formaldehyde is heated by an electric furnace in a flask with a cooler under atmospheric pressure in the presence of the active copper-bismuth catalyst. The temperature is regulated within $\pm 0.1^\circ\text{C}$. The rotation of the stirrer is about 300 r. p. m.. After the reaction system settles at a given temperature, the liquid samples are taken out at each given time interval in succession, and are analysed.

About 40 % aqueous formaldehyde solution is prepared from a commercial paraformaldehyde, and propargyl alcohol is synthesized in this laboratory³⁾. Various compositions of the liquid samples are made by adding a distilled water, methanol and butynediol to the aqueous formaldehyde solution and propargyl alcohol in compliance with experimental conditions. The pH value* is adjusted with sodium hydroxide and sulphuric acid.

Analyses of formaldehyde, propargyl alcohol and butynediol are performed by the sodium sulphite method, the silver nitrate method and the distillation method respectively

1) R. Kiyama, J. Osugi and K. Suzuki, *This Journal*, **22**, 22 (1952)

2) R. Kiyama, J. Osugi and K. Suzuki, *ibid.*, **22**, 65 (1952)

3) K. Suzuki, *ibid.*, **23**, 66 (1953)

* Beckmann pH-meter (glass electrode) is used.

as used in the previous work¹⁾. In this reaction butynediol is produced stoichiometrically according to Eq. (1). Therefore, the analysis of butynediol is not performed in all experiments and the amount of the butynediol formed is calculated from the consumed propargyl alcohol or formaldehyde. Moreover, the result that the amount of the tripple bond before and after the reaction is coincident from the analysis of the tripple bond⁴⁾, assures the consideration that the reaction proceeds according to Eq. (1).

Experimental Results

200 cc of the liquid sample and 130 cc of the cayalyst* are used in one experiment. The experiments are performed in the range of 70 ~ 100°C as the reaction temperature. The changes of reaction process under the conditions where formaldehyde concentration, propargyl alcohol concentration, pH, methanol content, butynediol concentration, etc. are changed, are investigated respectively. The experimental results obtained are classified and described according to the above mentioned experimental variables which are designated as the effect.

(1) Formaldehyde concentration effect

In the range of about 7 ~ 30 % formaldehyde concentration (A case), the concentration of the butynediol formed increases linearly against the reaction time. The rate of

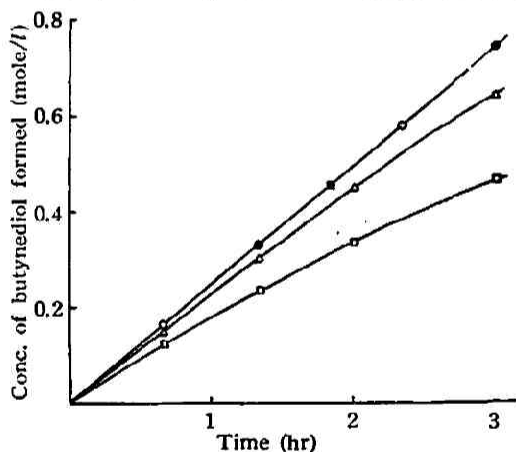


Fig. 1 Formaldehyde conc. effect

Formalde.
hyde %

○ 15.2	} ca. 7 % propargyl alc., pH 3.0, 98°C, Catalyst No. 2
● 23.0	
■ 29.6	
△ 36.3	
□ 4.7	

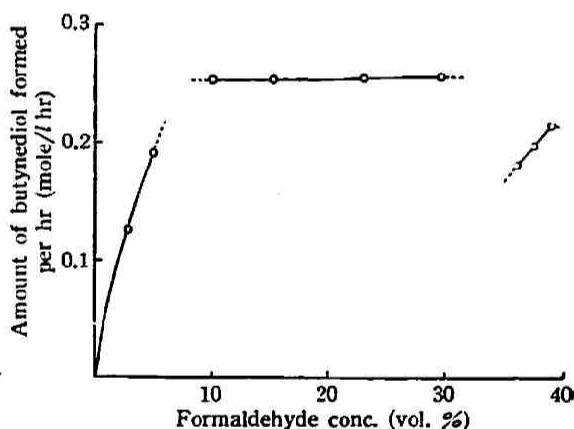


Fig. 2 Formaldehyde conc. effect

ca. 7 % propargyl alc.,
pH 3.0, 98°C,
Catalyst No. 2

4) K. Suzuki, *This Journal*, 23, 57 (1953)

* * The catalyst is one of the active copper-bismuth used in the previous work¹⁾. The same catalyst is used throughout this experiment, but the activity decreases during the long duration of its use. Experiments are performed in the cases of three kinds where the activity is the same in each case and the catalyst in each case is classified as Catalyst Nos. 1, 2 and 3 in order of its use.

butynediol formation, moreover, is equal irrespective of the formaldehyde concentration. But in the range below about 7 % (B case) and above about 30 % (C case) formaldehyde concentrations, the concentration of the butynediol formed does not increase linearly against the reaction time. The results which indicate these relations are shown in Fig. 1. Fig. 2 shows the relation between the formaldehyde concentration and the amount of the butynediol formed per hour.

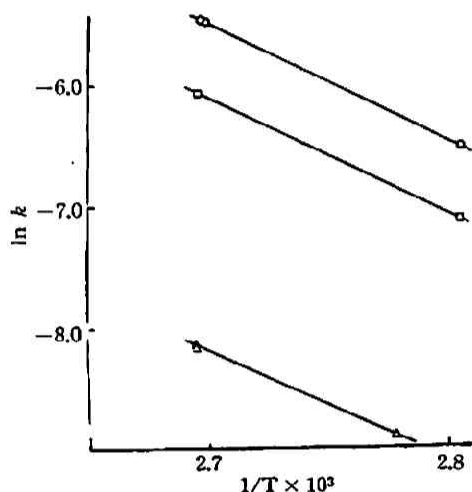


Fig. 3 Formaldehyde conc. effect

Formaldehyde %
 ○ 7~30 } ca. 7 % propargyl alc.,
 △ 35~40 } pH 3.0,
 □ below 7 } Catalyst No. 2

The experimental results of B and C cases show that the relations between the logarithm of formaldehyde concentration and the reaction time are linear, and so the rate of butynediol formation is the first order as to the formaldehyde concentration. Now, the rate constants in the zero or first order rate equation are 4.18×10^{-3} (zero order, mole/min), 2.44×10^{-3} and 2.86×10^{-4} (first order, min^{-1}) at 98°C in the cases of A, B and C respectively.

The rate of butynediol formation in each case is measured at different temperatures, and from the results obtained the relations between the logarithm of each rate constant $\ln k$ and the reciprocal of reaction temperature $1/T$ are shown in Fig. 3. And

17.8 kcal is obtained as the apparent activation energy irrespective of the formaldehyde concentration.

(2) Propargyl alcohol concentration effect

As shown in Fig. 4, the rate of butynediol formation are invariable irrespective of the concentration of propargyl alcohol. But when the concentration of propargyl alcohol is below 2 %, the rate equation of butynediol formation is not zero order even if the formaldehyde concentration lies in the range of A case. As the relation between the logarithm of propargyl alcohol concentration and the reaction time in this case is linear, it is found that the rate equation of butynediol formation is the first order as to the propargyl alcohol concentration.

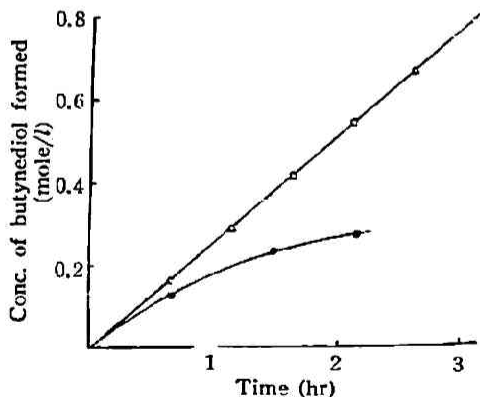


Fig. 4 Propargyl alc. conc. effect

Propargyl alc. %
 ○ 4.8 } ca. 20 % formaldehyde,
 △ 12.5 } pH 3.0, 98°C ,
 □ 28.5 } Catalyst No. 2
 ● 1.7 } ca. 13 % formaldehyde,
 pH 3.0, 98°C , Catalyst No. 1

(3) pH effect

In the experimental range performed, the rate of butynediol formation decreases with pH value. Some experimental results are shown in Fig. 5. From Fig. 6 which

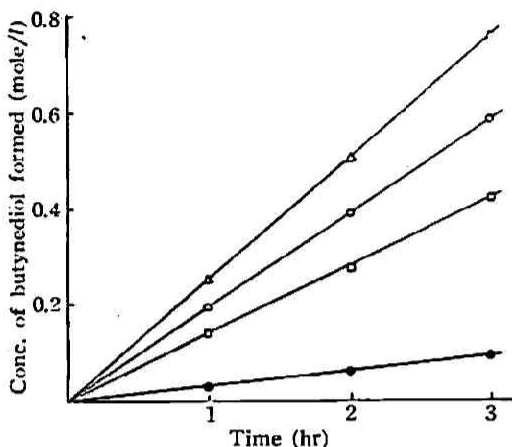


Fig. 5 pH effect

- Δ 4.3 } 13 % formaldehyde,
 \circ 3.0 } 7 % propargyl alc., 98° C.
 Catalyst No. 3
 \square 4.0 } 15 % formaldehyde,
 \bullet 1.5 } 7 % propargyl alc., 92° C.
 Catalyst No. 1

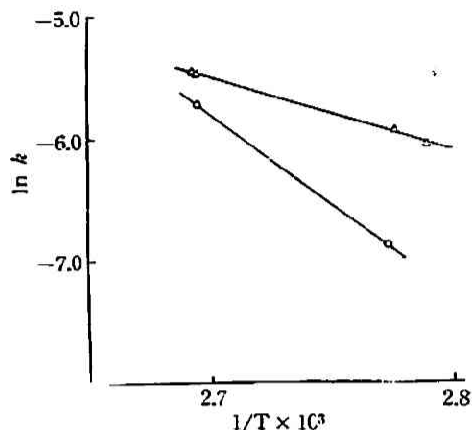


Fig. 6 pH effect

- Δ 4.3 } 13 % formaldehyde,
 \circ 3.0 } 7 % propargyl alc.,
 Catalyst No. 3

shows the relations between $\ln k$ and $1/T$, 12.4 and 29.7 kcal are obtained respectively as the apparent activation energy in the cases of pH 4.3 and 3.0. That is, the smaller the pH value is, the larger the value of activation energy becomes.

(4) Methanol effect

From the experiments under the conditions that various methanol contents are contained, the relations between $\ln k$ and $1/T$ obtained are shown in Fig. 7. The values of rate constant k vary with the methanol content, and the apparent activation energies of 17.8 and 37.2 kcal are obtained respectively in the cases of 0 and 20 % of methanol content (Catalyst No. 2) and also 11.6, 22.2 and 32.2 kcal respectively in the cases of 15, 28 and 40 % of methanol content (Catalyst No. 1)

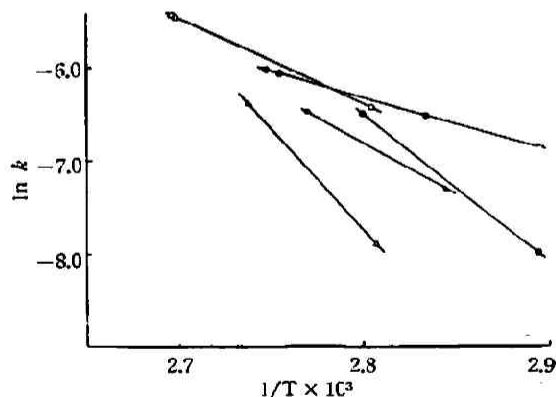


Fig. 7 Methanol effect

- Methanol
 %
 \circ 0 } 10 ~ 30 formaldehyde,
 Δ 20 } 7 % propargyl alc., pH 3.0,
 Catalyst No. 2
 \bullet 15 } 15 % formaldehyde,
 \blacktriangle 28 } 7 % propargyl alc., pH 4.0,
 \blacksquare 40 } Catalyst No. 1

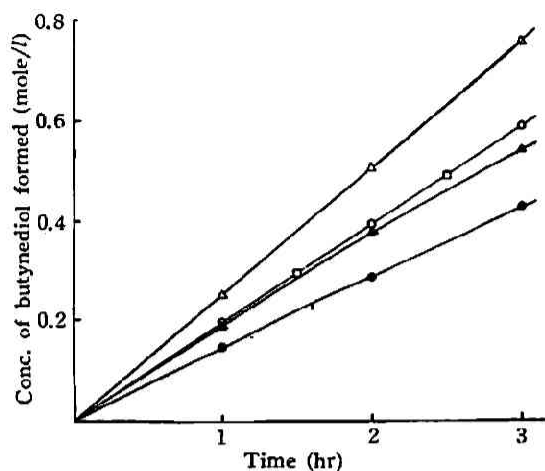


Fig. 8 Butynediol effect

Butyne- diol %	pH
○ 0	3.0
□ 5	"
● 20	"
△ 0	4.3
▲ 20	"

13 % formaldehyde,
7 % propargyl alc., 98 °C,
Catalyst No. 3

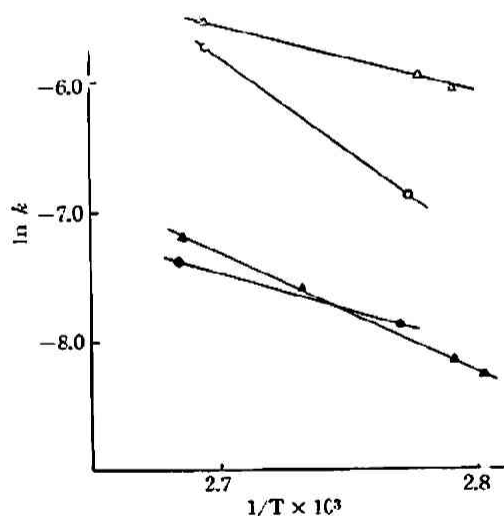


Fig. 9 Butynediol effect

Butyne- diol %	pH
○ 0	3.0
● 20	"
△ 0	4.3
▲ 20	"

13 % formaldehyde,
7 % propargyl alc.,
Catalyst No. 3

(5) Butynediol effect

Some results obtained in the case where butynediol is added previously to the initial sample are shown in Fig. 8. The rate of butynediol does not change as compared with the case where butynediol is not added. But in the case of the addition of 20 % butynediol, the rate of butynediol formation changes, and the reaction does not follow the zero order rate equation. Now, as the experimental results show the linear relations between the logarithm of formaldehyde concentration and the reaction time, it is found that the rate equation of butynediol formation is the first order as to the formaldehyde concentration. From the relations between $\ln k$ and $1/T$ shown in Fig. 9, the apparent activation energy in pH 3 decreases from 29.7 kcal (zero order) to 11.8 kcal (first order) by the addition of 20 % butynediol, while in pH 4.3 increases from 12.4 kcal (zero order) to 19.0 kcal (first order).

Considerations

The experimental results are classified and considered as follows.

(1) Formaldehyde concentration effect

As shown in the experimental results, in the range of about 7 ~ 30 % formaldehyde concentration (A case) where propargyl alcohol concentration is above about 2 %, the relations be-

tween the concentration of the butynediol formed and the reaction time are linear. That is, in this range the rate equation of the reaction is zero order, and butynediol is formed by the surface reaction. Namely, the rate of butynediol formation is expressed as follows:

$$\frac{d[B]}{dt} = k\theta_f\theta_p = k_{f_0}, \quad (2)$$

where $[B]$ is the concentration of butynediol in the solution, k and k_{f_0} are the rate constants, and θ_f and θ_p the fractions of formaldehyde and propargyl alcohol adsorbed on the catalyst surface respectively. In the case of A, the adsorption rates of formaldehyde and propargyl alcohol are greater than the surface reaction rate, and the reactants adsorb saturately on the catalyst surface, that is, θ_f and θ_p may be regarded as constant, therefore, the rate of butynediol formation is constant.

The fact that the rate of butynediol formation is the first order as to the formaldehyde concentration in the case below about 7 % (B case), is understood, considering that formaldehyde adsorbs unsaturately on the catalyst surface, and θ_f in Eq. (2) is proportional to formaldehyde concentration $[F]$ in the solution. That is,

$$\theta_f = k_f[F], \quad (3)$$

$$\frac{d[B]}{dt} = k\theta_f\theta_p = k k_f[F]\theta_p = k_{f_1}[F], \quad (4)$$

where

$$k k_f \theta_p = k_{f_1} = \text{constant}.$$

The rate equation of butynediol formation becomes the first order as to the formaldehyde in the range above about 30 % (C case). This fact is understood from the consideration that the nature of formaldehyde polymer would be changed in the neighborhood of 30 % formaldehyde concentration. It seems that the experimental result (C case) relates to the irregularity (in the vicinity of 30 % formaldehyde) of curve⁵⁾ indicating the relation between the partial pressure of formaldehyde in the aqueous solution at approximately 98 ~ 100° C and formaldehyde concentration.

As above mentioned, this reaction can be explained well as the surface reaction in any case. Moreover, this fact is assured by the following results: the rate of butynediol formation becomes half when the amount of liquid sample is twice, the rate of butynediol formation does not change even if the rotation of the stirrer becomes slow to 1/4 fold, and in any case the values of the activation energy are equally 17.8 kcal.

(2) Propargyl alcohol concentration effect

In the range above about 2 % propargyl alcohol concentration, the rate of butynediol formation is invariable irrespective of the propargyl alcohol concentration. This fact is understood from the consideration that propargyl alcohol adsorbs in saturation on the active points of the catalyst and θ_p in Eqs. (2) and (4) is invariable.

In the range below about 2 % propargyl alcohol where formaldehyde is about 7 ~ 30 % (A case), the rate equation of butynediol formation is the first order as to the propargyl alcohol concentration. This fact is understood, considering that propargyl

5) F. Auerbach and H. Barschall, *Studien über Formaldehyd*, Part 1 Formaldehyd in wässriger Lösung, p. 34 (1935); J. F. Walker, *Formaldehyde*, p. 55 (1944)

alcohol adsorbs unsaturately and θ_p in Eq. (2) is proportional to propargyl alcohol concentration $[P]$ in the solution, that is,

$$\theta_p = k_p[P], \quad (5)$$

$$\frac{d[B]}{dt} = k\theta_f\theta_p = k\theta_f k_p[P] = k_{p_1}[P], \quad (6)$$

where

$$k\theta_f k_p = k_{p_1} = \text{constant}.$$

(3) pH effect

The rate of butynediol formation decreases, and activation energy becomes large with the decrease of pH value. These facts are explained from the considerations that proton adsorbs on the more active point of the catalyst, and the activity of the catalyst contributing to the reaction becomes small by the decrease of pH.

(4) Methanol effect

The result that the activation energy increases with methanol content, is understood, considering that the activity of the catalyst decreases owing to the adsorption of methanol on the active point of the catalyst.

(5) Butynediol effect

In the range of concentration that the zero order reaction is established as to the concentrations of formaldehyde and propargyl alcohol, even if butynediol is formed by about 7% with the progress of the reaction the rate of butynediol formation is invariable and constant. And the rate of butynediol formation in the case of the addition of 5% butynediol does not either change as compared with the case where butynediol is not added. Thus, in the range below about 12% butynediol concentration, the retardation due to butynediol is not recognized in the reaction.

In the case of the addition of 20% butynediol, however, the rate of butynediol formation changes and becomes the first order as to the formaldehyde concentration even if the concentrations of formaldehyde and propargyl alcohol are in the range of zero order reaction.

The activation energy decreases in the case of pH 3.0 and increases in the case of pH 4.3 by the addition of 20% butynediol. It is difficult to discuss this problem further only from these experimental results.

Conclusions

The reaction of butynediol synthesis from propargyl alcohol and formaldehyde is studied in the presence of a catalyst under atmospheric pressure.

The rate equation of butynediol formation varies with the concentrations of formaldehyde and propargyl alcohol, and becomes zero order or the first order as to the concentration of formaldehyde or propargyl alcohol according to the condition. But the

rate determining step may be assumed to be the process of the surface reaction on the catalyst. Moreover, the changes of the surface reaction rate with pH, methanol content and the effects of butynediol on the reaction are investigated.

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